METHOD FOR WELDING STRIPS OF ALUMINIUM ALLOY

FIELD OF THE INVENTION

[01]   The invention relates to aluminum alloy strips coated on one or both sides with a brazing alloy, intended for manufacturing of brazed parts, and particularly heat exchangers for automobiles or buildings, and more particularly for parts assembled by fluxless brazing under a controlled atmosphere.

STATE OF THE ART

[02]   The use of structurally hardened core alloys for heat exchangers (particularly in the 6xxx series: Al-Mg-Si) was very frequent as long the vacuum brazing type process was used. This practice was terminated when the brazing technology changed and was replaced by brazing under a controlled atmosphere with Nocolok® non-corrosive flux, related to the high acquisition and maintenance costs of vacuum furnaces. The Nocolok® process imposes strict constraints on the use of magnesium alloys, since magnesium reacts with the flux used to dissolve the oxide layer, and makes it inoperative. The limit for the content is of the order of 0.3%. A very large amount of the flux would be necessary for higher contents, which would make the operation extremely expensive.

[03]   Moreover, the resistance to corrosion of a large number of strips for exchangers is based on the formation of an anodic layer at the core/cladding interface which imposes a very low content of silicon in the core. For example, this is the case of alloys described in patent EP 0326337 (Alcan).

[04]   Therefore 6xxx alloys were very largely replaced by 3xxx alloys with low magnesium and low silicon contents and the structural hardening effect was lost.

[05]   Type 3xxx core alloys with structural hardening were recently proposed, for example in patent EP 0718072 (Hoogovens Aluminum Walzprodukte) and in patent application EP 1254965 (SAPA Heat Transfer). In both cases, no modification has been made to the strips to improve their brazability in a standard Nocolok® furnace. Consequently, either

the magnesium content must be limited to a relatively low value (for example less than 0.35% as in the case of application EP 1254965), but the structural hardening effect is then reduced relatively small, or the quantity of flux deposited has to be increased or an alternative flux has to be used such as cesium flux described in patent US 5771962 (Ford). In both cases, this significantly increases the cost of the operation.

[06]   The invention is intended to propose a material that has structural hardening properties, and also good brazability in existing Nocolok® lines.

SUBJECT OF THE INVENTION

[07]   The subject of the invention is a process for the assembly of aluminum alloy sheets as defined above including fluxless brazing under a controlled atmosphere at a temperature of between 580 and 620°C, fast cooling and possibly aging at a temperature of between 80 and 250°C, and in which at least one of the plates is composed of a core alloy with the following composition (% by weight):

> Si 0.3 – 1.0;   Fe < 1.0;   Cu 0.3 – 1.0;   Mn 0.3 – 2.0;   Mg 0.3 – 3.0;   Zn < 6.0;   Ti < 0.1;   Zr < 0.3;   Cr < 0.3;   Ni < 2.0;   Co < 2.0;   Bi < 0.5; Y < 0.5; other elements < 0.05 each and 0.15 total, the remainder being aluminium, and coated on at least one face with an aluminium brazing alloy containing 4 to 15% of silicon and 0.01 to 0.5% of at least one of the Ag, Be, Bi, Ce, La, Pb, Pd, Sb, Y elements or mischmetal.

[08]   The following is a preferred composition for the core alloy:

> Si 0.3 – 1.0;   Fe < 0.5;   Cu 0.35 – 1.0;   Mn 0.3 – 0.7;   Mg 0.35 – 0.7;   Zn < 0.2;   Ti < 0.1;   Zr < 0.3;   Cr < 0.3;   Ni < 1.0;   Co < 1.0;   Bi < 0.5;   Y < 0.5; other elements < 0.05 each and 0.15 total, the remainder being aluminium,

[09]   When manufacturing heat exchangers, aging can be done during operation in the hot parts of the exchanger.

DESCRIPTION OF THE FIGURES

[10]   Figures 1a and 1b show top and side views respectively of V test pieces used in the examples to evaluate brazability.

[11]   Figure 2 shows the definition of the brazed joint width in the brazability test described in the examples.

DESCRIPTION OF THE INVENTION

[12]   The invention is based on the selection of a particular composition for the core alloy, for fluxless brazing, in combination with the addition of the cladding alloy containing one or several elements modifying its surface properties, such as the surface tension or the composition of the oxide layer.

[13]   The core alloy contains manganese and copper as well as silicon and magnesium to enable hardening of Mg_2Si by precipitation.

[14]   The silicon content must be more than 0.3% to enable the formation of a sufficient quantity of Mg_2Si, but it must remain less than 1% if a sufficient difference is to be maintained between the melting temperatures of the core alloy and the cladding alloy.

[15]   The magnesium content is between 0.3 and 3.0%, and preferably between 0.35 and 0.7%. It must be sufficient to enable the formation of Mg_2Si, and is not limited by the risk of reaction with the flux as in patent EP 1254965, since there is no flux. Unlike the teachings of patent application EP 1254965, the objective is not to achieve an excess silicon above the stoichiometric quantity to form Mg_2Si, but on the contrary an excess of magnesium is required. However, magnesium can have a negative effect on formability, consequently it is desirable to limit it to 0.7% for applications requiring extensive forming.

[16]   Copper increases the mechanical strength of the alloy when it is in solid solution. Unlike the teachings of EP 1254965, the applicant did not observe any reduction in the resistance

to corrosion beyond 0.3% provided that the value of 1% is not exceeded, since this is the limit at which copper precipitates. On the contrary, the presence of copper in solid solution increases the corrosion potential. Another reason for not exceeding 1% is to prevent the alloy melting temperature from dropping too much.

[17]   The cladding alloy is normally an aluminum alloy containing 4 to 15% of silicon, and possibly other additive elements such as Cu, Mg or Zn. One of the characteristics of the invention is that one or several elements are added to the cladding alloy to improve its wettability, from among the group composed of Ag, Be, Bi, Ce, La, Pb, Pd, Sb, Y and mischmetal, which is a mix of unseparated rare earth elements. This better wettability avoids the need to use a brazing flux, without operating under a vacuum.

[18]   The brazing alloy is usually clad onto the core alloy by co-rolling. If the brazing alloy is clad on a single face, the other face may be coated in a manner known by those of skill in the art by a sacrificial alloy, usually of the Al-Zn type designed to improve the resistance of the core alloy to corrosion.

[19]   The brazing alloy may also be deposited in the form of particles, particularly Al-Si particles, as for example described in patent EP 0568568 (Alcan International). For brazing under a controlled atmosphere, the brazing alloy particles are usually associated with flux particles, particularly a fluoride-based flux such as potassium fluoro-aluminate, and a binder such as a polymer resin. In this case, one particular advantage of the invention is to avoid the presence of a flux in the coating.

[20]   Between 0.05 and 0.5% bismuth and/or 0.01 to 0.5% yttrium may also be incorporated in the core alloy.

[21]   Fluxless brazing may be done under a controlled atmosphere, for example nitrogen or argon, at a temperature of between 580 and 620°C, which enables melting of the brazing alloy and also enables dissolution of the core alloy. This dissolution is followed by fast

cooling, for example with blown air. The assembled part can be aged at a temperature of between 80 and 250°C.

[22]   For the manufacture of heat exchangers, it is sometimes possible to perform the aging during operation in the hottest parts of the exchanger, for example for automobile engine cooling radiator tubes.

EXAMPLE

[23]   Several core alloy plates were cast with the compositions shown in Table 1:

Table 1									
Alloy	Si	Fe	Cu	Mn	Mg	Ti	Bi	Y	Ca
M	0.40	0.22	0.63	0.57	0.47	0.08	-	-	-
M + Bi	0.39	0.22	0.62	0.59	0.49	0.09	0.15	-	-
M + Y	0.39	0.24	0.61	0.57	0.47	0.09		0.05	-
M + Ca	0.40	0.22	0.63	0.57	0.47	0.08	-	-	0.05

and plates of 4047 (Al-12%Si) cladding alloy or 4047 + 0.19% Bi cladding alloy or 4047 + 0.05% Y cladding alloy or 4047 + 0.05% Ca cladding alloy. Assemblies are made from these plates such that the thickness of the cladding alloy is equal to 10% of the total thickness. These assemblies are hot rolled, and then cold rolled so as to produce 0.3 mm thick clad strips. The strips are subject to a recovery heat treatment for 10 h at 260°C.

[24]   The test piece depicted in Figure 1 was used to evaluate the brazability of these materials. The « V » is composed of a 0.3 mm thick bare strip made of 3003 alloy in the H24 temper. A 15-minute degreasing treatment at 250°C is applied to the metal to be brazed. No other surface preparation is applied and in particular no flux is deposited. Brazing is done in a double wall glass furnace so that liquid brazing movements and the formation of joints during the treatment can be viewed. The thermal cycle is composed of a rising temperature phase up to 610°C at a rate of about 20°C/min, a 2-minute holding phase at 610°C, and a falling temperature phase at a rate of about 30°C/min. The entire operation is done under continuous scavenging by nitrogen at a rate of 8 l/min.

[25]   A mark from A to E is assigned to the results, according to the following scale:

Mark	A	B	C	D	E
Joint length formed as a percentage of the total length	100%	90%	75%	50%	0%

Table 2 contains the results:

Table 2		
Core	Cladding	Brazability
M	4047	E
M	4047 + Bi	B
M + Bi	4047 + Bi	A
M + Y	4047 + Y	B
M	4047 + Ca	E

[26]   The mechanical characteristics are measured on the M/4047+Bi, M+Bi/4047+Bi and M+Y/4047+Y composites together after brazing, and after various aging treatments. Table 3 shows the values obtained and compares them with an alloy N conventionally used for strips for use in heat exchangers with the following composition:

Alloy	Si	Fe	Cu	Mn	Mg	Ti
N	0.19	0.15	0.68	1.38	-	0.08

Table 3				
Composite	State	R_m (MPa)	$R_{0.2}$ (MPa)	A (%)
M/4047 + Bi	After brazing	202	95	9.3
M/4047 + Bi	After brazing + 4 h at 180°C	236	169	5.8
M/4047 + Bi	After brazing + 8 h at 180°C	236	191	3.3
M + Bi/4047 + Bi	After brazing	210	100	8.4
M + Bi / 4047 + Bi	After brazing + 4 h at 180°C	231	172	4.8
M + Bi / 4047 + Bi	After brazing + 8 h at 180°C	245	196	4.1

Table 3				
Composite	State	R_m (MPa)	$R_{0.2}$ (MPa)	A (%)
M + Y / 4047 + Y	After brazing	207	95	9.4
M + Y / 4047 + Y	After brazing + 4 h at 180°C	240	170	6.4
M + Y / 4047 + Y	After brazing + 8 h at 180°C	256	198	5.2
N/4045	After brazing	166	64	18.0
N/4045	After brazing + 4 h at 180°C	164	60	16.9
N/4045	After brazing + 8 h at 180°C	163	60	17.0

[27]   The very favourable effect of structural hardening on the mechanical strength, particularly after aging, can be seen clearly.